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(54) Method and apparatus for producing thin film of compound having large area.

(57) A thin film of a compound having a large area is continuously produced on a substrate by depositing elements constituting the compound from a target member onto the surface of substrate by spattering comprising steps of:

rotating a target member having a flat surface around an axis which crosses the surface and comprising elements of the compound so that a part of the surface of target member is positioned at a first spattering position and another part of the target member is positioned at a second spattering position,

at the first position, spattering at least one target comprising at least one element of the compound which is easily splashed so as to supply the deficient element to the target member, and

at the second position, spattering the elements from the target member so as to deposit them on the surface of said substrate with continuously supplying the substrate so that a part of the substrate is positioned in a flying line of the elements,

whereby an elementary composition of the target member at the second position is adjusted at a predetermined composition.

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METHOD AND APPARATUS FOR PRODUCING THIN FILM OF COMPOUND HAVING LARGE AREA

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method and an apparatus for producing a thin film of a compound having a large area. More particularly, it relates to a method for producing a thin film of a compound on an elongate substrate or a large substrate by spattering the compound on a continuously supplied substrate to form a thin film of the compound on the substrate, and an apparatus for carrying out said method.

Description of the Related Art

A superconductive phenomenon which is said to be a phase transition of electrons is a phenomenon in which a conductor has zero electric resistance and exhibits complete diamagnetism under specific conditions.

In electronic engineering which is one of technical fields in which the superconductive phenomenon can be utilized, various superconductive devices have been and are proposed and developed. One of the typical devices is an element utilizing the Josephson effect in which the quantum effect is macroscopically exhibited by applied current. Since the superconductor has a small energy gap, a tunnel junction type Josephson element comprising the superconduc tor is expected as a high speed switching element with small power consumption. Further, since the Josephson effect appears as an exact quantum phenomenon against electromagnetic wave or magnetic field, a Josephson element will be used as a very high sensitive sensor for sensing magnetic field, microwave, radiation, etc.

Since, in a very high speed computer, power consumption per unit area almost reaches the limit of cooling capacity, it is highly desired to provide superconductive elements. In addition as a degree of integration in an electric circuit is increased, it is expected to use a superconductor as a wiring material with little or no current loss.

In spite of enormous efforts, critical temperature Tc of the superconductor could not have exceeded 23K of Nb_3Ge for a long time.

In these years, a sintered material of an oxide such as $(La,Ba)_2CuO_4$ or $(La,Sr)_2CuO_4$ was found to be a superconductor with high Tc and is expected to realize high temperature superconductivity. In such oxide superconductors, Tc of 30 to 50 K and sometimes Tc of 70K or higher is observed.

In addition, a composite oxide of the formula: $Y_1Ba_2Cu_3O_{7-w}$ which is referred to as "YBCO" is reported to be a 90K grade superconductor. Further, a Bi-Sr-Ca-Cu type and Tl-Ba-Ca-Cu type composite oxides not only have Tc higher than 100K, but also is chemically stable so that its superconductive properties are less deteriorated as time passes while the superconductive properties of YBCO may be deteriorated as time passes.

Since the oxide superconductor is prepared as a sintered material, it is usually brittle and requires great care in handling. That is, the ceramic oxide superconductor is easily broken or cracked by mechanical stress. Particularly, the ceramic oxide superconductor in the form of a wire is very easily broken. Therefore, its practical use has severe limitation.

Furthermore, it is very difficult to form a sintered superconductor from homogeneous polycrystal consisting of particles all having superconductive characteristics and, as a general property of the superconductor, the superconductive state may be locally broken by fluctuation of external magnetic field or cooling temperature. The ceramic oxide superconductor has smaller thermal conductivity and larger electrical resistance than the classical superconductors. Therefore, when the superconductive state is locally broken, such part of the superconductor is locally heated by electrical current which flows through the superconductor. If the cooling medium contacts the locally heated part of superconductor, it is explosively vaporized.

To prevent such explosive vaporization, the classical metal superconductor is processed in the form of a thin filament and a plural number of filaments are bundled by a good conductive material such as copper, which acts as a thermal conductor and a by-pass of electric current in case of breakage of superconductive state. However, it is difficult to process the ceramic oxide superconductor produced by sintering and having high Tc in the form of filament.

To produce the wire or filament form oxide superconductor, it seems to be essential to continuously form a thin film of the superconductor.

As a result of the extensive study, the present inventors have found that a spattering method in which the superconductive material is used as a target is most suitable for forming a practically applicable thin film of the oxide superconductor.

However, since the oxide superconductor comprises several elements having different vapor pressures, adsorption probabilities and reaction

rates, a composition of the compound formed on the substrate differs from that of the target, or the elementary composition on the surface of the target varies during spattering.

When the thin film is formed on an elongate substrate or a large substrate, it takes a long time to form the thin film on the whole surface of the substrate. Therefore, the composition of the target varies during spattering, when the compound itself is used as the target.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a method for continuously producing a thin film of a compound, particularly a ceramic oxide superconductor, having a large area on a substrate.

Another object of the present invention is to provide a method for producing a thin film of a compound having a homogeneous composition on a substrate.

A further object of the present invention is to provide an apparatus for continuously producing a thin film of a compound, particularly a ceramic oxide superconductor, having a large area on a substrate.

According to the first aspect of the present invention, there is provided a method for continuously producing a thin film of a compound having a large area on a substrate by depositing elements constituting the compound from a target member onto the surface of substrate by spattering comprising steps of:

rotating a target member having a flat surface around an axis which crosses the surface and comprising elements of the compound so that a part of the surface of target member is positioned at a first spattering position and another part of the target member is positioned at a second spattering position,

at the first position, spattering at least one target comprising at least one element of the compound which is easily splashed so as to supply the deficient element to the target member, and

at the second position, spattering the elements from the target member so as to deposit them on the surface of said substrate with continuously supplying the substrate so that a part of the substrate is positioned in a flying line of the elements,

whereby an elementary composition of the target member at the second position is adjusted at a predetermined composition.

According to the second aspect of the present invention, there is provided an apparatus for continuously producing a thin film of a compound having a large area on a substrate comprising:

a chamber internal pressure of which is reduced to high vacuum,

means for supplying an atmospheric gas into the chamber,

first spattering means for supplying at least one element constituting the compound to a target member having a flat surface around an axis which crosses the surface and comprising elements of the compound by spattering at least one target comprising said element, and

second spattering means for depositing elements constituting the compound from the target member onto the surface of substrate in the chamber,

wherein the target member is circulated between a first position at which the first spattering is carried out and a second position at which the second spattering is carried out.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 schematically shows an apparatus to be used for forming a thin layer of an oxide superconductor on a substrate according to the present invention,

Fig. 2 schematically shows a right side subroom of the chamber in which magnetron spattering is used for supplying a deficient element, and

Fig. 3 schematically shows a right side subroom of the chamber in which a metal rod is heated in vacuum by a heater which surround the rod to supply a deficient element.

DETAILED DESCRIPTION OF THE DRAWINGS

The method and apparatus of the present invention are suitable for producing a thin film of an oxide superconductor, particularly, an oxide superconductor having a composition of the formula:

$$(M^1_{1-x}M^2_x)M^3_yM^4_z \quad (I)$$

wherein M^1 is at least one element selected from the IIa group elements, M^2 is at least one element selected from the IIIa group elements, M^3 is at least one element selected from Ib, IIb, IIIb, IVa and VIIIa group elements , M^4 is at least one element selected from the group consisting of oxygen, boron, carbon, nitrogen, fluorine and sulfur, x is an atomic ratio of M^2 to (M^1+M^2) and from 0.1 to 0.9 and y and z are atomic ratios of M^3 and M^4 to (M^1+M^2) and from 1.0 to 4.0 and from 1 to 5, respectively.

Preferred examples of the IIa group element M^1 are Ba, Sr, Ca, Mg and Be, particularly Ba and Sr. It is preferred that 10 to 80 % of the element M^1 comprises at least one of Mg, Ca and Sr. Preferred examples of the IIIa element M^2 are Y and lanthanoids (e.g. La, Sc, Ce, Gd, Ho, Er, Tm,

Yb and Lu), particularly Y, La and Ho. It is preferred that 10 to 80 % of the element M^2 comprises at least on of Sc and lanthanoids. Generally, the element M^3 is Cu, although a part of the element M^3 may be replaced with at least one element selected from the Ib, IIb, IIIb, IVa and VIIIa group elements, preferably T and V.

Preferred examples of the oxide superconductor (I) are $Y_1Ba_2Cu_3O_{7-w}$, $La_1Ba_2Cu_3O_{7-w}$, $La_1Sr_2Cu_3O_{7-w}$, $Ho_1Ba_2Cu_3O_{7-w}$, $Nd_1Ba_2Cu_3O_{7-w}$, $Sm_1Ba_2Cu_3O_{7-w}$, $Eu_1Ba_2Cu_3O_{7-w}$, $Gd_1Ba_2Cu_3O_{7-w}$, $Dy_1Ba_2Cu_3O_{7-w}$, $Er_1Ba_2Cu_3O_{7-w}$ and $Yb_1Ba_2Cu_3O_{7-w}$ wherein w is larger than 0 (zero) and smaller than 1 (one).

The method and apparatus of the present invention are also suitable for producing a thin film of a superconductor comprising a mixed phase or a single phase of a composite oxide having a composition of the formula:

$M^5_p(M^6_{1-q},Ca_q)_mCu_nO_{r+s}$ (II)

wherein M^5 is Bi or Tl, M^6 is Sr when M^5 is Bi or Ba when M^5 is Tl, p is 4, m is from 6 to 10, n is from 4 to 8, r is (3p+2m+2n)/2, q is larger than 0 (zero) and smaller than 1 (one), and s is from -2 to 2.

Specific examples of the superconductor (II) are $Bi_4Sr_4Ca_4Cu_6O_{20+s}$, $Bi_2Sr_2Ca_2Cu_3O_{10+s}$, $Tl_4Ba_4Ca_4Cu_6O_{20+s}$ and $Tl_2Ba_2Ca_2Cu_3O_{10+s}$.

As the substrate on which the thin film of the compound is formed, any metallic substrate can be used. Examples of the metallic substrate are those made of stainless steel, Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb and alloys thereof. Among them, Cu and Fe are preferred since they are inexpensive and easily processed. Pt is also preferred since it is stable and chemically inactive against the oxide superconductor. Further, Ag, Pd and Rh are advantageous as a substrate material particularly for the oxide superconductor which requires control of an oxygen content, since some kinds of their oxides liberate oxygen by temperature change. Preferably, the surface of substrate made of these materials, is coated with ZrO_2 or MgO. This is because the critical current density of the oxide superconductor has crystal anisotropy. When the oxide superconductor is formed on the layer of Zr_2O or MgO, its crystal has orientation in a direction of the c axis so that the critical current density can be increased and a current direction in which the critical current density is large can be controlled.

To supply the deficient element to the target member at the first position, any of physical deposition methods can be used. Particularly, ion beam spattering is preferred.

The second spattering of the compound onto the substrate can be carried out by any of conventional spattering methods. Among them, magnetron spattering is preferred.

It is preferred to heat the substrate at a temperature of 500 to 1,000°C. It is also preferred to post heat the formed thin layer of the oxide superconductor in an oxygen-containing atmosphere at a temperature of 500 to 1,000°C and to anneal the oxide superconductor by cooling it at a cooling rate of 10°C/min. or less. By annealing, oxygen defects in the oxide superconductor crystal are removed so that the superconductive properties are improved.

In the apparatus of the present invention, the easily splashable element is supplied to a part of the target member at the first spattering position and then said part of the target member is circulated to the second spattering position at which all the elements are spattered to deposit them on the surface of the substrate. Then, said part is returned to the first position and the element is supplied thereto. Therefore, each part of the target member which is moved to the second position contains all the elements in a desired ratio, and the thin film of the compound with a homogeneous composition can be formed continuously on the elongate or large substrate.

The target member is preferably in the form of a cylinder or a disc and circulated between the first and second spattering positions by rotation. When the first and second spattering positions require different spattering conditions such as atmosphere, the chamber of the apparatus is partitioned by a wall into two subrooms, and the target member is circulated between two subrooms with keeping the atmosphere of each subroom by differential exhaust.

In the present invention, the substrate is preferably of linear form such as a tape or a sheet and continuously supplied in the chamber of the spattering apparatus.

According to the present invention, the composition of the target member can be kept constant for a long time, and it is possible to form the homogeneous thin layer of the compound on a whole length of a continuously supplied elongate substrate.

One of particularly advantageous application of the present invention is production of a linear form oxide superconductor.

PREFERRED EMBODIMENTS OF THE INVENTION

Preferred embodiments of the present invention will be illustrated by way of example by making reference to the accompanying drawings.

Example 1

By the method of the present invention, a thin film of an oxide superconductor having a composition of $Ba_2YCu_3O_7$ was formed on an elongate tape made of stainless steel.

An apparatus used in this Example is schematically shown in Fig. 1.

The apparatus of Fig. 1 comprises a spattering chamber 1, at a substantially center position of which, a disc shaped target member 2 is installed. The target member consists of a sintered oxide material a composition of which is adjusted by taking the formation of the thin film by RF spattering into consideration.

A wall divides the chamber 1 into two subrooms. In a left side subroom, spattering of the compound is carried out to form a thin film of the compound on a stainless steel tape 4. To this purpose, a magnet 5 is placed beneath the target member 2 to establish magnetron conditions. On a right side of the wall, a pair of ion beam spattering apparatuses 6a and 6b and a pair of targets 7a and 7b are positioned to supply the deficient elements to the target member 2.

The target member 2 rotated at a predetermined rate. In the left side subroom, it is used as a source member for spattering the compound onto the substrate, and then it is supplied with the deficient element(s) in the right side subroom.

In case of spattering of a Ba-Y-Cu composite material, Y tends to remain in the target member, while Ba is most easily splashed. Therefore, in this Example, Cu and Ba were supplied from the targets 7a and 7b, respectively.

When the RF spattering is effected in the right side subroom, high frequency fills the whole chamber 1. Therefore, some measure should be taken to prevent the spattering induced by such high frequency in the left side subroom. To this end, ion beam spattering under highly reduced pressure is preferred to supply the deficient elements in the right side subroom. The supplied amounts of the elements can be controlled by adjusting accelerating voltages of ion sources and gas pressure in the chamber 1. Preferably, pressure in the right and left side subrooms is adjusted independently from each other by installing an independent exhausting means to each subroom. In the apparatus used in this Example, a rotary pump and an oil diffusion pump are connected to each subroom, and pressure is reduced to around 10^{-3} Torr by the rotary pump and then precisely controlled by the oil diffusion pump.

The parameters and conditions used in this Example were as follows:

(1) Target member (disc form)
Sintered material of BaY_2CuO_7
Outer diameter: 15 inches
Inner diameter: 7 inches
Applied output power: 10 W/cm^2
Rotation speed: 0.5 rpm
Deposition rate: 10Å/sec.

(2) Spattering conditions on the substrate
Magnetic field: 300 G on the substrate surface
Substrate temperature: 700 °C
Partial pressure of argon: 8×10^{-3} Torr
Partial pressure of oxygen: 2×10^{-3} Torr

(3) Spattering conditions for supplying deficient element
Target 7a: Cu
Target 7b: Ba
Vacuum: 5×10^{-4} Torr (argon)
Accelerating voltage:
Ion source 6a: 4 kV
Ion source 6b: 5 kV

The target disc member 2 may be produced as follows:

A mixture of powdery oxides, carbonates, nitrates or sulfates of Ba, Y and Cu in a predetermined weight ratio is molded in a suitable shape and then sintered at a high temperature according to a conventional method. Preferably, after the molded mixture is presintered, it is ground, molded and again sintered.

Although in the above Example the ion beam spattering was used for supplying the deficient elements, any other suitable methods can be used for supplying the deficient elements. Further, not only Ba and Cu but also Y can be supplied so as to more precisely control the growing rate of the thin film of the compound and/or the elementary composition of the compound.

Fig. 2 schematically shows another embodiment of a right side subroom of the chamber 1 in which magnetron spattering is used for supplying a deficient element to the target member 2. A magnetron electrode 9 is installed over the target member 1 and connected to a high frequency source 8. In the electrode 9, the target 7 for the deficient element is positioned.

Fig. 3 schematically shows a further embodiment of a right side subroom of the chamber 1 in which a metal rod 10 (for example, a copper rod) is heated in vacuum by a heater 11 which surround the rod 10 to evaporate the metal and deposit it on the target member 2 for supplying the deficient element (for example, copper).

Example 2

By using the apparatus of Fig 1, a thin layer of an oxide superconductor having a composition of $Bi_4Sr_4Ca_4$-Cu_6O_{20+s} was formed on an elongate tape made of stainless steel having a layer of ZrO_2 on the surface.

In case of spattering of a Bi-Sr-Ca-Cu composite material under the same conditions, Sr and Ca tend to remain in the target member, while Bi is most easily splashed. Therefore, in this Example, Bi and Cu were supplied from the targets 7a and 7b, respectively.

The parameters and conditions used in this Example were as follows:

(1) Target member (disc form)
Sintered material of $Bi_4Sr_4Ca_4Cu_6O_{20+s}$
Outer diameter: 15 inches
Inner diameter: 7 inches
Applied output power: 10 W/cm^2
Rotation speed: 0.5 rpm
Deposition rate: 10 Å/sec.

(2) Spattering conditions on the substrate
Magnetic field: 300 G on the substrate surface
Substrate temperature: 700°C
Partial pressure of argon: 8 x 10^{-3} Torr
Partial pressure of oxygen: 2 x 10^{-3} Torr

(3) Spattering conditions for supplying deficient element
Target 7a: Bi
Target 7b: Cu
Vacuum: 5 x 10^{-4} Torr (argon)
Accelerating voltage:
Ion source 6a: 4 kV
Ion source 6b: 5 kV

The disc shape target member 2 was prepared by sintering a mixture of Bi_2O_3 powder, $SrCO_3$ powder, $CaCO_3$ powder and Cu powder in such ratio that an atomic ratio of Bi:Sr:Ca:Cu was 2:2:2:3 by a conventional method.

The present invention is not limited to the above illustrated embodiments.

When the thin film of the oxide superconductor is formed on a large area substrate, a shielding member can be produced. When a masking element is positioned over the substrate or a drum and the thin film of the oxide superconductor is formed through the make, a coil for superconductive magnet can be produced.

Claims

1. A method for continuously producing a thin film of a compound having a large area on a substrate by depositing elements constituting the compound from a target member onto the surface of substrate by spattering comprising steps of:

rotating a target member having a flat surface around an axis which crosses the surface and comprising elements of the compound so that a part of the surface of target member is positioned at a first spattering position and another part of the target member is positioned at a second spattering position,

at the first position, spattering at least one target comprising at least one element of the compound which is easily splashed so as to supply the deficient element to the target member, and

at the second position, spattering the elements from the target member so as to deposit them on the surface of said substrate with continuously supplying the substrate so that a part of the substrate is positioned in a flying line of the elements,

whereby an elementary composition of the target member at the second position is adjusted at a predetermined composition.

2. The method according to claim 1, wherein the target member is in the form of a cylinder or disc and rotated around an axis of the cylinder or a center of the disc.

3. The method according to claim 1, wherein the compound to be spattered is an oxide superconductor having a composition of the formula:

$$(M^1{}_{1-x}M^2{}_x)M^3{}_yM^4{}_z \quad (I)$$

wherein M^1 is at least one element selected form the IIa group elements, M^2 is at least one element selected from the IIIa group elements, M^3 is at least one elements selected from Ib, IIb, IIIb, IVa and VIIIa group elements, M^4 is at least one element selected from the group consisting of oxygen, boron, carbon, nitrogen, fluorine and sulfur, x is an atomic ratio of M^2 to (M^1+M^2) and from 0.1 to 0.9 and y and z are atomic ratios of M^3 and M^4 to (M^1+M^2) and from 1.0 to 4.0 and from 1 to 5, respectively.

4. The method according to claim 1, wherein the substrate on which the thin film of the compound is formed is a metallic substrate made of a metal selected from the group consisting of stainless steel, Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb and alloys thereof.

5. The method according to claim 1, wherein the substrate comprises a non-metallic base material coated with a layer of a metal selected from the group consisting of stainless steel, Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb and alloys thereof.

6. The method according to claim 1, wherein the spattering at the first position consists of ion beam spattering.

7. The method according to claim 1, wherein the spattering at the second position consists of magnetron spattering.

8. The method according to claim 1, wherein the substrate is heated at a temperature of from 230 to 1,410 °C during spattering.

9. The method according to claim 1, wherein the substrate is heated at temperature of from 230 to 1,410 °C after forming the thin film of the compound thereon.

10. An apparatus for continuously producing a thin film of a compound having a large area on a substrate comprising:

a chamber internal pressure of which is reduced to high vacuum,

means for supplying an atmospheric gas into the chamber,

first spattering means for supplying at least one element constituting the compound to a target member having a flat surface around an axis which crosses the surface and comprising elements of the compound by spattering at least one target comprising said element, and

second spattering means for depositing elements constituting the compound from the target member onto the surface of substrate in the chamber,

wherein the target member is circulated between a first position at which the first spattering is carried out and a second position at which the second spattering is carried out.

11. The apparatus according to claim 10, wherein the target member is in the form of a cylinder or disc and rotated around an axis of the cylinder or a center of the disc.

12. The apparatus according to claim 10, wherein the first spattering means is an ion beam spattering apparatus.

13. The apparatus according to claim 10, wherein the second spattering means is a magnetron spattering apparatus.

FIG.1

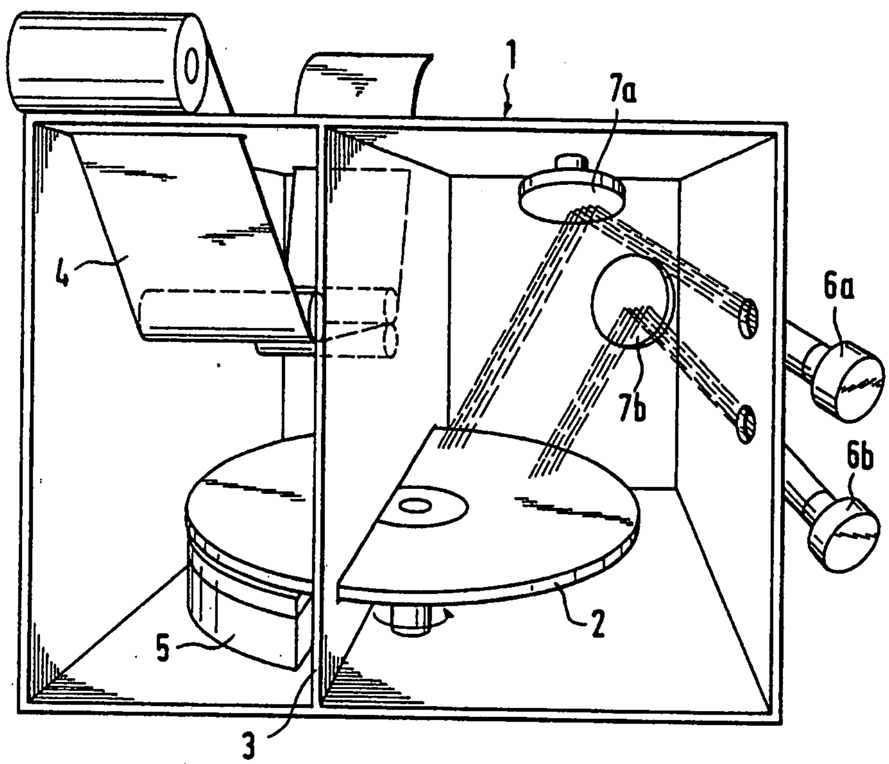

FIG.2

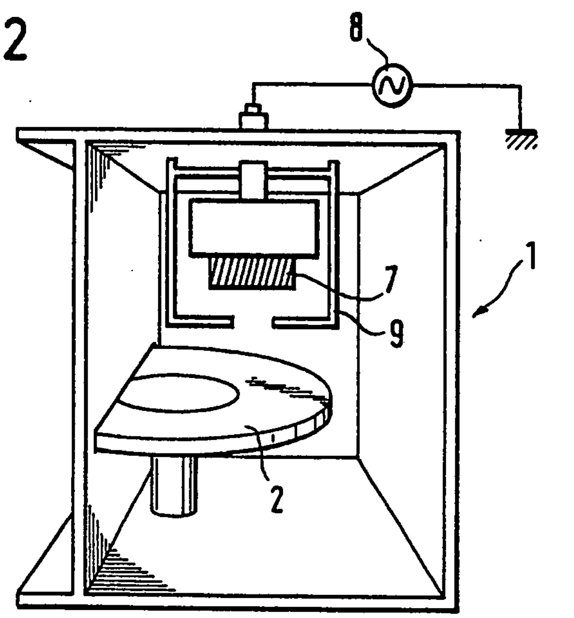

FIG.3